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Study of the plasma immersion implantation of titanium in stainless steel

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Abstract. The results of the study of the pulsed plasma-immersion ion implantation of titanium in steel Cr18Ni10Ti depending on the time (dose) implantation are presented. It is shown that the change of the element and the phase composition of the surface layers and their microscopic characteristics and mechanical properties (hardness, wear resistance) depending on the implantation time is not monotonic, but follows to a certain rule. The possibility of interpretation of the obtained results in the thermal spike concept of the generation on the surface by the stable (magic) clusters is discussed. This concept follows logically from the recent studies on the plasma arc composition and from a polyatomic clusters-surface interaction.

1. Introduction

The plasma-immersion implantation is a comparatively new method of the properties modifying of the near surface layers of solids, is widely used recent times. It is connected with the modification of the physical, chemical and mechanical properties of the surface layers, formation new compounds including intermetallic compounds (obtaining and study of which is constitute the separate wide sector in the chemistry and metallurgy) [1–3]. All this is very important for many areas of modern technologies (from micro- and nano-electronics to metallurgy) [4].

Plasma immersion implantation at the 1–10 keV energies of implanting ions is realized from metal plasma arc, when the implanted metals uses as the cathode of the arc discharge source. Impulse voltage is served to implantable sample (target for implanted ions) to accelerate the positive ions of the plasma without overheating the target. In this work the implantation was carried out on the installation developed in Tomsk Polytechnic University by the authors of [5]. The main advantages of the installation called by the authors "Raduga-5" is a high speed set-dose implanted ions [6]. In this work the objects of the study was Cr18Ni10Ti steel is used in equipment for oil industry, chemical plants and equipments, which are resistant to high temperatures. The strength and the wear resistance increase during the implantation titanium ions into the steel [7,8] which leads to growing operating time.

The purpose of the work was to study the microstructure, the distribution of elements and phases formed in the surface layers of the modified material depending on the dose of implanted ions and the study of the mechanical properties obtained by implantation of surface layers.

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2. Materials and Methods

The Cr18Ni10Ti steel was used as the modified material (target). Implanted samples surface has a size 25x25x1 mm, which was polished. Titanium (VT1-00, technically pure, rus) has been used as the cathode of the arc plasma source. The arc current was I = 90 A. The amplitude of the voltage pulses applied to the target was U = -2 kV relative to the ground (anode of the arc evaporator); the pulse length was t_{imp}=7 μs; the pulse frequency was ν =100 Hz; the ion current density per pulse was J= 6.5 $mA\cdot cm^{-2}$; the temperature of the implanted surface rises to 900 °C for 5 minutes, which was measured using a pyrometer. The Auger electron spectrometer "Shuna-2" and the glow discharge spectrometer GD-PROFILER-2 were used for researching distribution of elements in the depth of the modified layers. The X-ray diffractometer Shimadzu XRD 7000 was used for researching phase composition of the surface layers. Photographs of the microstructure were obtained by using the three-dimensional non-contact profilometer MicroMeasure 3D Station optical microscope with a camera 30 KB S Pruftechnik GmbH and scanning electron microscope-3000 TM. Mechanical properties of the surface were investigated using the nanohardness NANOHardness Tester NHT-S-AX-000X and the high temperature tribometer PC-Operated HighTemperature Tribometer TNT-S-AH0000.

3. Results and discussion

The concentration profiles of Fe (a) and Ti (b) are shown in fig. 1, which are depending on the implantation time of titanium in steel 18Cr10NiTi (numbers about the curves show implantation time). There are profiles of Cr, Ni, C, N and O which were obtained on a glow discharge GD-PROFILER 2, and for determining the concentration were calibrated according to the Auger electron spectrometer "Shuna-2."

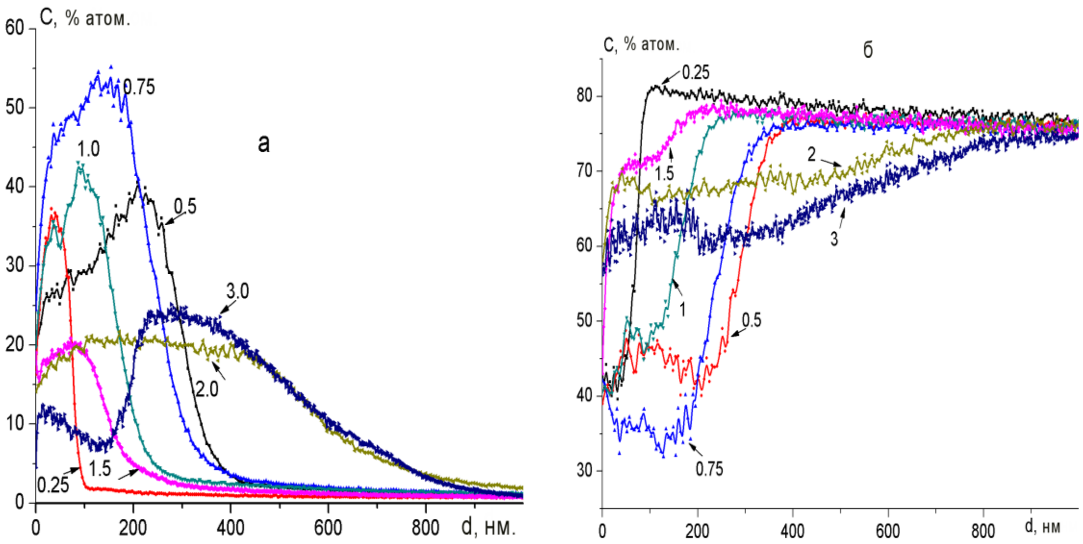


Figure 1. Concentration profiles of titanium (a) and iron (b) after the implantation of titanium in steel Cr18Ni10Ti. The numbers on the curves show the time of implantation in minutes.

From the fig. 1a follows that the modification profile of titanium can be described as the accumulation in the surface layer (up to 400 nm) with increasing irradiation time from 0.25 to 0.75 min. Broadening and shifting the profile to 800 nm with increasing the irradiation time of up to 2 or 3 minutes is observed. The curves at 2 and 3 minutes of irradiation are very similar to the thermal diffusion profiles. Profiles with irradiation time 1 and 1.5 min fall from the described trends. Note that the same fallings of the trends are observed in the study of other methods (see below): phase analysis,

microhardness, and friction coefficient. Therefore, you should not talk about the experimental error in the measurement but about the features of implantation technology.
Fig. 2 shows the phase composition of the surface-modified stainless steel after 3 minute of irradiation. It is seen that the intermetallic compound are formed on the surface. However, the composition of the compounds changes from irradiation time. The TiNi and Fe_2Ti intermetallics absent at the 0.5 min and 0.75 min implantation time. The TiNi compound fixed only at the 1 min and 3 min implantation time. Line intensity of these phases changes with increasing implantation time without any regularity.

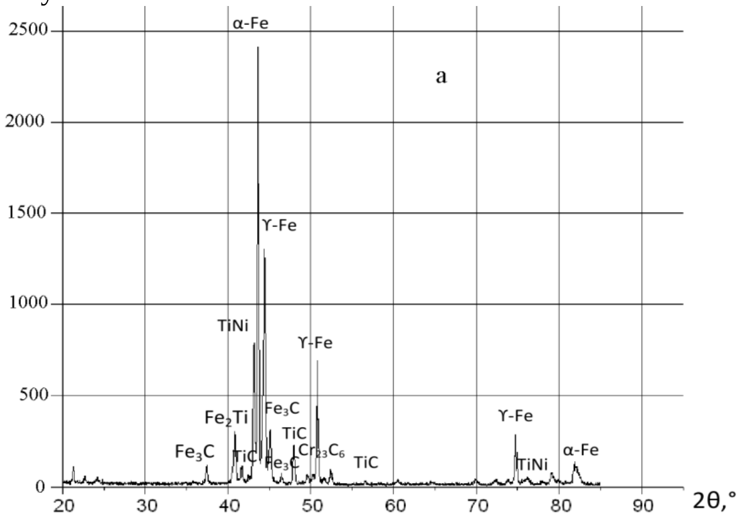
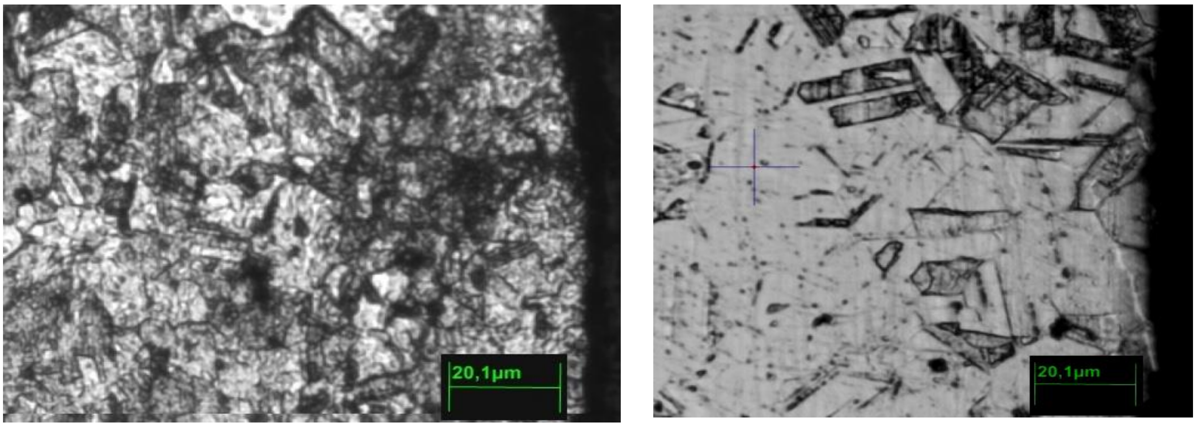


Figure 2. The surface diffractograms of the Cr18Ni10Ti implanted steel

The optical pictures of a perpendicular metallographic grinding of the steel samples are shown on the fig. 3. Metallographic were made simultaneously on all samples (including unimplanted) using epoxy resin which was poured in a metallic cylindrical shell.



a **b**

Figure. 3. Optical images of thin surface layer of metallographic sections of steel after titanium implantation: a) initial; b) implantation time 3 min.

Therefore, the dark layers on the photos are the hardened epoxy resin has penetrated between samples. From Fig. 3 it is seen that grain structure of the near surface layer of steel varies, grains are elongated needle appearance with the increasing of the implantation time. This change is traced in all modified samples independent of dose.

The initial and modified samples were taken for the study of wear resistance of the modified surface on the tribometer «High Temperature Tribometer». High-temperature tribometer is used for measuring friction coefficient, wear resistance, wear rate in different temperature conditions, in a gas atmosphere and lubricating liquids. The velocity of the contact zone along the track was 2 $cm \cdot s^{-1}$, number of circles was 1000. The measurement results of the friction coefficient are shown in Table 1.Wear track area was measured using the three-dimensional profilometer Micro Measure 3D Station. Nine track squares and the arithmetic mean values were obtained for each sample. Results are presented in Table 2.

Table 1. The dependence of the friction coefficient from the implantation time titanium in steel.

Implantation time, min	Friction coefficient
0	0.437
0.25	0.320
0.5	0.506
1	0.490
1.5	0.494
2	0.236
3	0.168

The friction coefficient decreases at the 2 and 3 min implantation time. The wear track square for samples with the 0.25, 0.5, 0.75, 2, and 3 min implantation time is less than the initial sample. Accordingly the wear resistances of these samples are increased.

Table 2. Dependence of the arithmetic mean value of the wear track square from the implantation time of titanium.

	Implantation time, min							
	Initial	0.25	0.5	0.75	1	1.5	2	3
The arithmetic means of the square track wear μm^2.	605	84	126	266	667	747	53	49

From the above it follows that the optimal time of 2 and 3 min for obtaining the lowest friction coefficient and wear track square. The study of the microhardness and the wear resistance of the samples repeated the trends described above, i.e. the trend change of the surface microhardness occurs, but it is not monotonic.

Fig. 4 shows the example of the microhardness changing from the penetration depth of the indenter for the modified samples (the numbers near color curvers show the implantation time in minutes). These regularities may be related to effects such as the presence cluster and (or) microdroplet fraction in a flow of charged metal plasma; the effects of erosion and growth surface during implantation (thermal peaks, oversputtering layers created in the previous steps) and others. It is clear that it is impossible to evaluate the role of each of these effects at this study step for this technology.

However, it is known for example that the formation time of the thermal peak is 10^{-10}–10^{-9} s, and the its relaxation time is 10^{-10} s for monocharged and monoatomic ions [9]. The surface cannot be warmed up when the irradiation conditions such as at the pulse frequency of 100 Hz, the time between the arrival of pulses to the surface is ~10^{-2} s. The formation process of intermetallic compounds during the existence of the thermal peak requires high temperatures and pressures. The temperature in the heat peak can achieve ~1000 ^{0}C when the surface is bombarded such ions (monocharged and monoatomic) so the ion energy should be considerably higher than in the experiments presented here. Therefore it is

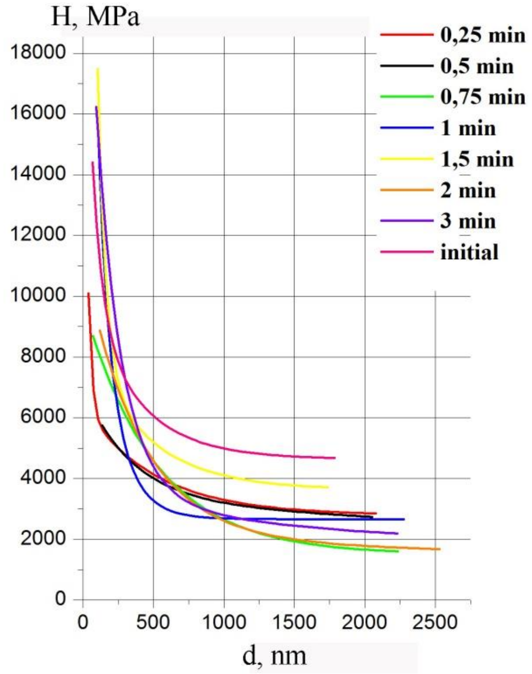
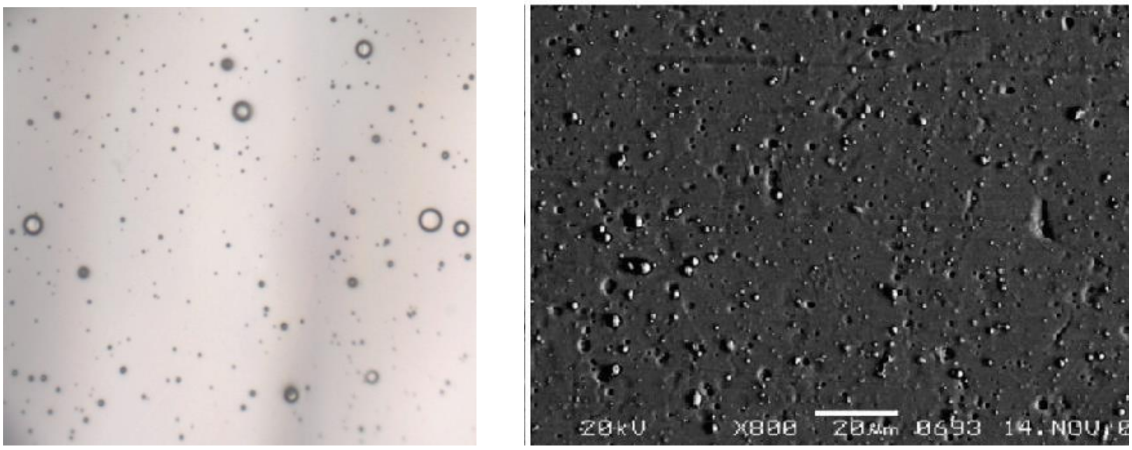


Figure 4. Dependence nanohardness from the indenter depth in Cr18Ni10Ti steel .

necessary to pay attention to lack of sufficient information about the presence of clusters with the N ≥100 number of atoms in the composition of the arc plasma. The fact that in [10] in studying the interaction of such clusters with the surface, provided that the collision energy per atom is E_{col}≥10 eV (this condition holds in our experiment) the following was established. In the collision zone for a short time (≤500 fs) from the beginning of the interaction creates a medium characterized by the temperature of ~10^4–10^5 °C, the density of atoms in the 4–5 times higher than the density of the solid and the pressure P≥1 Mbar [10]. Many physical and chemical processes that are impossible in equilibrium conditions are possible in such conditions (the formation of intermetallic compounds and even nuclear reactions). Argue that the plasma of arc discharge under certain conditions (especially the presence in it of an inert "buffer" gas; in our experiments such gas is argon) is a cluster plasma allow the results [10–13]. In these works the review of theoretical and experimental studies of the plasma clusters (including plasma of arc discharge [13]) and original theoretical results presented by the authors. In our experiment, we are dealing with beam of the cluster plasma can be argued on the basis of these studies. The hot clusters [11] play a crucial role in the modification of the surface. Cluster sizes can vary between a few atoms up to several thousand atoms (microdroplets fraction). Но до мишени долетают только стабильные ("магические" [12]) кластеры. Only stable ("magic" [12]) clusters reach the target with a high probability. In the case of titanium (densely packed hexagonal lattice) magic numbers of atoms in a cluster can be 1, 13, 57, 153, 321, 581, etc. [12]. Metal magic) cluster can carry a positive charge, at least from the 1e to 3e. Charged cluster becomes even more stable [13]. Cluster mechanism of surface modification confirmed by Fig. 5, which shows the image of the surface after plasma immersion implantation. Fig. 5a shows the optical image obtained on the microscope 30 KB S PruftechnikGmbHso 100X lens after implantation in our apparatus (in this experiment). Fig. 5b is taken from [14] in which the experiment is completely similar to ours, but the installation Platit π -80.This image obtained by the scanning electron microscope JEOL JSM6060A (Japan). Fig. 5a and 5b clearly views as microdroplets and the craters dimensions from a few microns to a disappearing small. We did not have the technical capabilities to make pictures with the increase of greater than in Figure 5 at the time of writing.

The images that are presented in Fig. 5, completely correspond to the described above concept of a cluster surface modification. They allow the following interpretation.



a **b**

Figure 5. Microscopy image of the surface of stainless steel after the plasma-immersion implantation in plants "Raduga-5" (a) и Platit π -80 (б) [14].

Microdroplets are the result of effects on the surface of the hot liquid clusters with number more than 1000 atoms; craters are formed by Magic clusters with the number of atoms less than 1000.

Conclusion

The increase in the friction coefficient and microhardness, reducing the surface wear resistance and the formation of intermetallic compounds show the great prospects for the pulse plasma immersion implantation for the surface modification. On the other hand, the data show that the charged clusters are the major contributors to the modification.

Further experiments on plasma immersion implantation should be aimed at clarifying the dependence of plasma flow on the parameters of the arc discharge.

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